

CLARIFICATION

RECOMMENDED METHODS FOR MEASURING TOC IN SEDIMENTS

Prepared by Kathryn Bragdon-Cook (Department of Ecology) for the PSDDA agencies.

INTRODUCTION

Current PSEP protocols for measuring total organic carbon (TOC) in sediment call for drying a sediment sample at 70 degrees C in order to minimize the loss of volatile organic compounds. HCl is then added to the dried sample to remove inorganic carbon and dried again at 70 degrees C. The sample is then combusted using cupric oxide fines as a catalyst at 950 degrees C. A preweighed, ascarite-filled tube is used to capture the resulting CO₂ upon combustion. The tube is then weighed once more to determine the concentration of CO₂ which is used to calculate the TOC in percent dry weight based on total solids in the sample.

Ecology's Technical Information Memorandum, "Organic Carbon Normalization of Sediment Data", recommends Methods 5310A-D, slightly modified, from the 18th Edition of Standard Methods for the Examination of Water and Wastewater (Franson, 1992). These include a wet chemical oxidation method (5310D) and a combustion method (5310B), both using infrared detection (IR). The Department of Ecology Manchester Environmental Laboratory recommends Method 5310B for measuring TOC in wastewater or, with some modification, in sediments. Test Methods for Evaluating Solid Waste (EPA 1986) SW-846 Method 9060 also references Standard Methods for the Examination of Water and Wastewater for measuring TOC levels of solid and hazardous waste.

These methods require some modification for measuring TOC in sediment. Standard Method 5310B calls for the sample to be treated with HCl to convert inorganic carbon to CO₂ which is then purged using purified gas. The sample is homogenized and diluted as necessary. A portion is injected with a blunt-tipped syringe into a heated reaction chamber (packed with a catalyst) of a carbon analyzer using infrared detection. Needle size is selected to be consistent with particle size. Some accredited laboratories have adapted this technique to sediment by drying the sample at 70 degrees C and using an instrument attachment to the carbon analyzer designed specifically for sediment samples (Dohrman sludge/sediment boat sampler attachment, Model 183, for use with the Dohrman DC-80 TOC analyzer). The sample is then combusted and organic carbon in the sediment converted to CO₂ and transported in carrier gas streams to be measured by an infrared detector.

Method 5310D describes the wet-oxidation method where the sample is acidified and purged as above and oxidized with persulfate in an autoclave from 116 to 130 degrees C. Again, the resultant CO₂ is measured by infrared spectrometry. Adaptation of this method to sediments may be problematic. Reagents and analytical techniques may be adjusted by the laboratory, however, to increase oxidation of organic carbon in sediments.

The carbon analyzer/infrared detection used in these methods identifies characteristic spectral fingerprints as light in the infrared spectrum passes through various molecules. This instrument offers greater sensitivity than the ascarite-filled tube collector for measuring low levels of CO₂.

PROBLEM IDENTIFICATION

The combustion method dries the sediment sample at 70 degrees C to minimize the loss of organic compounds, but 70 degrees C is not enough to drive off all of the moisture in the sample. A minimum

temperature of 104 degrees C is needed to ensure a truly dry sample for total solids calculations. At 104 degrees C, however, a significant loss of volatile organics occurs.

In addition, the ascarite-filled tube used to detect CO₂ in the PSEP method is less sensitive than the infrared detector of the standard methods, limiting accurate detection of low TOC concentrations. Comparative data between the two methods are not yet available.

PSDDA Reports, Development of Sediment Quality Values for Puget Sound, lists the 50%, 75%, and 90% TOC percentile concentrations for Puget Sound at 1.31%, 2.30%, and 4.50% respectively. TOC levels for individual test sites, however, vary greatly with some concentrations well below these averages. Low level detection of TOC in these areas is less accurate using the PSEP method.

Because the Ecology sediment clean up program and PSDDA program may overlap on projects, the need exists for consistency in the method used to measure TOC in sediments.

PROPOSED ACTION/MODIFICATION

Standard Method 5310B and SW-846 Method 9060 provide for more sensitive measurement of TOC concentrations in sediment. SW-846 Method 9060 (as modified by Laucks Laboratories for example) can detect TOC in sediments below 0.1%. Analytical precision for the PSEP method is not given in the protocols. For these reasons, utilization of Method 5310B or SW-846 Method 9060 using infrared detection is strongly recommended. Under conditions described below the PSEP method is acceptable.

Based on the lack of analytical error data for the PSEP method and greater instrument sensitivity of the combustion/IR method, the following guideline is given.

Prior to method selection, consideration should be given to the condition of the test site regarding probable TOC levels. When possible, historical data of particular sites should be reviewed to identify probable TOC concentration ranges.

When TOC concentrations are above 2% either method described could be used. Standard Method 5310B or SW-846 Method 9060 should be used for areas where TOC levels below 2% are likely. PSDDA applicants should state in their sampling and analysis plan which method for measuring TOC in sediment is proposed and provide detailed justification.

To correct for true dry weight with either method, the corresponding total solids analysis should be run twice, once at 70 degrees C and once at 104 degrees C, and the TOC calculation based on dry weight at 104 degrees C.

This document serves as an addendum to Ecology's Technical Information Memorandum (TIM) noted above. An errata sheet to replace page 3 of this TIM can be obtained by calling the Department of Ecology.

REFERENCES

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